"SYNTHESIS AND CHARACTERISATION OF ACTIVATED CARBON AND ITS STUDY ON Cr (VI) REMOVAL FROM WATER"

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By

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CERTIFICATE:

This is to certify that the thesis entitled, “Synthesis and characterisation of activated carbon and its study on Cr (VI) removal from water”, submitted by Soumya Ranjan Pati, Roll No.-108CH017, in partial fulfilments for his requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is prepared by him under my supervision and guidance.

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Soumya Ranjan Pati

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NOMENCLATURE

^0C	: Degree Celsius
BET	: Brunnauer Emett Teller
Cr	: Chromium metal
MOF	: Metal Organic Framework
nm	: Nanometer
H_3PO_4	: Phosphoric acid
KOH	: Potassium hydroxide
K_2CO_3	: Potassium carbonate
EPA	: Environment Protection Agency
$ZnCl_2$	: Zinc chloride
HCl	: Hydrochloric acid
NaOH	: Sodium hydroxide
SEM	: Scanning electron microscope
UV	: Ultra-violet
κ	: Kappa number
$KMnO_4$	: Potassium permanganate
A	: Volume of $KMnO_4$ used in the solution
A_0	: Spectral intensity at time t=0
A_c	: Spectral intensity at the end of the reaction
Q_c	: Quantity of cellulose in mg from standard curve
D	: Dilution test factor
ASTM	: American Society for Testing and Materials
M	: Moisture content
A	: Ash content

VM : Volatile matter

FC : Fixed carbon

P_0 : Saturation pressure of the adsorbate

P : Equilibrium pressure of the adsorbate

v : Volume of gas adsorbed

v_m : Volume of gas adsorbed in the monolayer

c : BET constant

E_1 : Heat of adsorption for the first layer

E_L : Heat of adsorption for higher layers

R : Universal gas constant

T : Absolute temperature

N : Avogadro's number

s : Adsorption cross-section of the gas being adsorbed

V : Molar volume of the gas being adsorbed

X : Mass of the adsorbent

FTIR : Fourier Transform Infra-Red

KBr : Potassium Bromide

rpm : Revolutions per minute

C_0 : Initial concentration

C_e : Equilibrium concentration

q_e : Adsorption capacity

mg/g : Milligram per gram

TGA : Thermo-Gravimetric Analysis

ABSTRACT

A novel approach for the synthesis and characterization of activated carbon was used. Precursor used for the synthesis of the activated carbon was a mixture of coconut and bael fruit shells. Lignin and cellulose content of the precursor were determined. Chemical activation of the precursor was done using phosphoric acid. Carbonization was carried out in a tube furnace at 450 ^{0}C under N_2 atmosphere for 1 hour. The study was made for varying ratios of coconut and bael fruit shells at an acid concentration of 30%. Also, the effect of acid concentration and activation temperature on yield and BET surface area was made. The surface area was determined using BET analyzer using liquid nitrogen. The specific surface area for activated carbon synthesized from pure coconut and pure bael fruit shells were also determined. Characterization and application of the activated carbon was done for the sample prepared from bael and coconut shells in 1:2 ratio. The effect of activation temperature and acid concentration on yield of the activated carbon were studied. The activated carbon sample was used to study the Cr (VI) ion removal efficiency from water. The effect of various parameters like pH, adsorbent dosage, temperature and initial concentration of Cr (VI) on the Cr (VI) removal efficiency was studied. Langmuir, Freundlich and Temkin adsorption models were fitted to the experimental data.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION:

Adsorption is a unit operation which refers to attachment of molecules to a surface. It is based on the fact that some solids have the inherent ability to preferentially attach certain substances from the solution onto their surfaces. It is widely used in industrial units to remove hazardous impurities and objectionable odors from industrial gases. In liquid operations, it is used in the removal of various heavy metals from water, decolorization of petroleum products etc. The substance which is used for the removal of certain substances during the process of adsorption is called adsorbent and the substance being adsorbed is called adsorbate. The process of adsorption is broadly divided into two categories depending on the type of forces involved between adsorbent and adsorbate-physiorption and chemisorption. Physiorption involves intermolecular forces of attraction between the adsorbent and the adsorbate. It is based on the simple fact that all molecules exhibit attractive forces. Due to the difference in concentration of the adsorbate between the solution and the adsorbent, the adsorbate migrates through the pore structure to reach the point of maximum attractive forces and gets deposited on the surface. Chemisorption involves chemical bonding or interaction between the adsorbent and the adsorbate.

In general most of the solids have the capacity of adsorption. But very few of them have the capacity of being used as a commercial adsorbent. A number of adsorbents are currently used in laboratories and industries for various applications. Activated carbon, silica gels, activated alumina, metal organic framework (MOF) being some of the notable ones. Large specific surface area i.e. surface area per unit mass is the most desirable property of an adsorbent. For example, a typical gasmask charcoal has an effective surface area of 100000 m^2/kg [1]. Bulk of this surface area is attributed to the large surface of the internal pores of the particles. These pores can be classified into three categories [2]:

- Micropores- <2 nm
- Mesopores- 2-50 nm
- Macropores->50 nm

The adsorbents are quite specific in their ability to adsorb substances depending on the pore size and size of the molecules being adsorbed.

Many commercial adsorbents are available today. However increased pollution levels and superior performance ability of adsorbents in pollution abatement has led to increasing demands of adsorbents. Thus newer materials are being sorted to meet the increasing demands of the adsorbents. Activated carbons are one of the oldest class of adsorbents known to mankind. They are a special class of carbonaceous materials which have been specially treated to create a highly developed internal pore structure. This improved pore structure is responsible for the superior performance of the activated carbons. They are used in the abatement of hazardous contaminants, treatment of municipal and industrial wastewater, as catalyst orcatalyst support in medicine, and the recovery of valuable metals [3].

The raw material used for the synthesis of activated carbons is any organic material having high carbon content. These raw materials are further activated using special techniques to give activated carbons. Broadly, the activation process can be divided into two classes- physical activation and chemical activation. Physical activation involves carbonization of the raw material followed by activation using steam, carbon dioxide or air [4-7]. Chemical activation involves impregnation of the raw materials using a chemical reagent like H_3PO_4, KOH and K_2CO_3 [8-10].

Activated carbons are very well suited to water pollution abatement. They are used in water filters for removal of objectionable odors and organic contaminants from water. They have

been found to be very effective in the removal of heavy metal ions like cadmium, chromium, lead and mercury from water [11]. Cr ions are one of the most toxic heavy metals discharged into water, predominantly from steel and pulp mills, electroplating, paint and photography industries. High levels of chromium ions in water may lead to liver damage, ulceration and skin irritation [12]. Cr ions are present in different oxidation states Cr(VI) being the most stable and most toxic form. As per the EPA standards, potable water should have a Cr(VI) ion concentration less than 0.05 mg/l[13]. Several methods have been used for the treatment of waste water containing chromium ions. Ion exchange, reverse osmosis, electrochemical reduction and direct precipitation are few of the methods used for this purpose [14-15]. Most of these methods are expensive and need high capital investment. Activated carbons provide a cost effective alternative in this regard and hence adsorption is the most widely used process for the removal of Cr (VI) ions from water. This has led to the search for low cost feedstock as raw materials for the synthesis of activated carbons. A number of studies have been made for the synthesis of activated carbon from organic waste which include that from walnut shell [16], coconut shell [17], peachstones [18], sugarcane bagasse [19], etc. Activated carbons prepared from coconut shells [20], hazelnut shell [21], *Terminalia arjuna* nuts [22], have been successfully demonstrated for the removal of chromium ions from water.

Coconut shells are by far the most predominantly used precursor for the production of activated carbons due to its abundance in the environment. Coconut shells have been found to yield microporous activated carbons [23]. Precursors having lower lignin content tend to yield activated carbons of high microporosity [24]. The purpose of this study is to decrease the lignin content of the coconut shell based precursor by mixing it with another precursor having lower lignin content (i.e. bael fruit shell) thereby increasing the microporosity of the activated carbon.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Extensive studies have been carried out by various authors for the synthesis and characterisation of activated carbons from different feedstocks. The following table gives a brief review of the various raw materials that have so far been used for the production of activated carbons.

Table 1: List of raw materials which have been used for the production of activated carbon

Raw materials	**Authors**
Rubber-seed shell	Sun K., Jiang J.[3]
Walnut shell	Hu Z., Vansant E.F. [16]
Coconut shell	Laine J., Calafat A., Labady M.[17]
Peachstones	Caturla F., Molina-Sabio M., Rodríguez-Reinoso F. [18]
Sugarcane bagasse	Girgis B.S., Khalil L.B., Tawfik T.A.M. [19]
Hazelnut shell	Kobya M. [21]
Terminalia arjuna nuts	Mohanty K., Jha M., Meikap B.C., Biswas M.N. [22]
Camellia oleifera	Kang S., Jian-chun J., Dan-dan C.[25]
Corn Cob	Tsai W.T., Chang C.Y., Wang S.Y., Chang C.F., Chien S.F., Sun H.F. [26]
Rubber wood sawdust	Srinivasakannan C., Bakar M.Z.A.[27]

In the production of activated carbons from walnut shells, the walnut shells were first carbonized mixed with KOH solution and the mixture was activated thermally in absence of air. The products were washed with water and dried to get the final activated carbon. The effect of activation temperature, activation time and KOH/char ratio on the development of microporosity were studied [16].

In case of coconut shell based activated carbons; coconut shell was ground and sieved to a size range of 0.2-0.5 mm, impregnated with phosphoric acid and carbonized in a muffle furnace for 1 hour. Then the product was cooled, washed with water, filtered and dried at 120 ^{0}C. Carbonization was also carried out under controlled flow conditions in a tube furnace at a heating rate of 10 ^{0}C/ min at the required temperature for 1 hour. The effect of carbonization temperature was studied and best results were obtained at 450 ^{0}C. The surface area increased with increase in concentration of the phosphoric acid [17].

In case of rubberwood sawdust, two stage activation procedure was followed. The predried sawdust was mixed with required ratio of 60 % phosphoric acid and allowed to remain soaked overnight. The samples were then put in a muffle furnace at 200 ^{0}C for 15 min. for semi-carbonization. The sample was taken out and put in a dessicator and put again in the furnace when the desired activation temperature was reached in the furnace. After activation, the samples were taken out of the furnace, washed first with distilled water and then with 0.1 M NaOH solution and dried in an oven at 105 ^{0}C. Semi-carbonization at 200 ^{0}C for 15 min. was followed by activation at 500 ^{0}C for 45 min. With impregnation ratio of 1.5, a product with maximum iodine number of 1096 mg/g and surface area of 1496 m^2/g and yield of 35% was obtained [27].

In another study with coconut shell activated carbons, the coconut shell was grounded and sieved to the size range of 0.6 mm to 1 mm. The precursor was impregnated with $ZnCl_2$ in

1:1 weight ratio and kept at 80 ^{0}C for 14 hours. Pyrolysis was carried out at constant N_2 flow rate of 5l/hour in an oven at 500 ^{0}C for 3 hours. The samples were then washed and dried at 110 ^{0}C for 3 hours. A part of this sample was further activated by physical activation. The temperature was raised to 900 ^{0}C under N_2 flow rate. At 900 ^{0}C, steam was passed through the sample for 30 min. Chemically activated only samples had lower surface areas than the samples subjected to both physical and chemical activation [28].

Numerous studies have been carried out to study the removal of Cr (VI) from water using activated carbon prepared from different sources. The following table shows the precursors used so far for this purpose by various authors.

Table 2: List of raw materials which have been used for the production of activated carbon to study Cr (VI) removal from water.

Raw materials	**Authors**
Coconut shell	Babel S., Kurniawan T. A. [20]
Hazelnut shell	Kobya M. [21]
Terminalia arjuna nuts	Mohanty K., Jha M, Meikap B.C., Biswas M.N. [22]
Palm shell	Owlad M., Aroua M.K., Wan Daud W.M. [29]
Peanut shell	AL-Othman Z.A., Ali R., Naushad M. [30]

In case of coconut shell based activated carbons, surface modifications was done in the activated carbons using oxidizing agents such as sulphuric acid, nitric acid and chitosan. The surface modified samples showed better adsorption capacity for Cr (VI) ions. This is due to the development of negative surface charge on the surface of the adsorbent which tends to favour the adsorption of Cr (VI) ions on the adsorbent surface. Effect of adsorbent dosage, pH, agitation speed, and contact time were studied [20].

Activated carbons synthesized from hazelnut shell were used to study the effect of pH, initial concentration and temperature on the removal of Cr (VI) ions from water. The adsorption capacity was found to decrease with increase in pH from 1-8 which showed that acidic conditions tend to favor the adsorption of Cr (VI) ions. The adsorption capacity increased with increase in temperature. Cr (VI) adsorption occurred rapidly at lower concentrations of Cr (VI). Pseudo first order model was fitted to the experimental data. Equilibrium was achieved rapidly with low initial concentration of Cr (VI) ions [21].

Palm shell based activated carbon has been successfully used for the production of high surface area activated carbons. The activated carbon was produced by physical activation using steam as the activation agent. The synthesized activated carbon was used to study the removal efficiency of Cr (VI) from water. The effect of low molecular weight polyethyleneimine loading on the activated carbon, pH, and concentration of Cr (VI) on Cr (VI) adsorption was studied. The activated carbon modified with polyethyleneimine was found to be very effective for the removal of Cr (VI) removal from water as it was found to have high adsorption capacity for Cr (VI). The adsorption data best fitted the Freundlich adsorption model [29].

The nature of activation in case of activated carbons depend on three major factors-

- Chemical impregnation ratio
- Activation duration
- Activation temperature

Chemical impregnation ratio: - It is the ratio of the weights of the chemical agent and the dry precursor [31]. Dehydrating agents are predominantly used as chemical agents in chemical activation which facilitate the development of the tiny pores. These tiny pores result in higher surface area of the activated carbons. Increase in concentration of the impregnant results in more development of micropores which leads to increase in surface area till an optimum is reached. Further increase in concentration of the chemical agent leads to the development of meso and macropores which do not contribute to the surface area significantly [32].

Activation duration: - It refers to the time period for which the sample is carbonized in the tube furnace at the desired temperature. During carbonization, volatiles and moisture are removed from the samples thus leading to the development of pores.

Activation temperature: - It refers to the temperature at which the sample is carbonized in the tube furnace. Higher temperature leads to more and more removal of volatiles and better development of pores.

The following table shows the optimum conditions for the above three parameters as predicted by various authors.

Table 3: Optimum activation conditions for different precursors

Precursor	**Author**	**Chemical impregnation ratio**	**Activation duration (min.)**	**Activation temperature (^{0}C)**
Rubber-seed shell	Sun K., Jiang J. [3]	-	60	880
Rubber wood sawdust	Srinivasakannan C., Bakar M. Z. A. [27]	1.5	45	500
Coconut shell	Gratuito et al.[31]	1.725	19.5	416
Peanut hulls	Girgis et al.[33]	1	-	-
Grain sorghum	Diao et al.[34]	-	14	600 for 1 stage 500 for 2 stages
Cassava peel	Sudaryanto et al.[35]	5:2	-	750
Date stone	Haimour N.M., Emeish S. [36]	0.4	60	800

CHAPTER 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

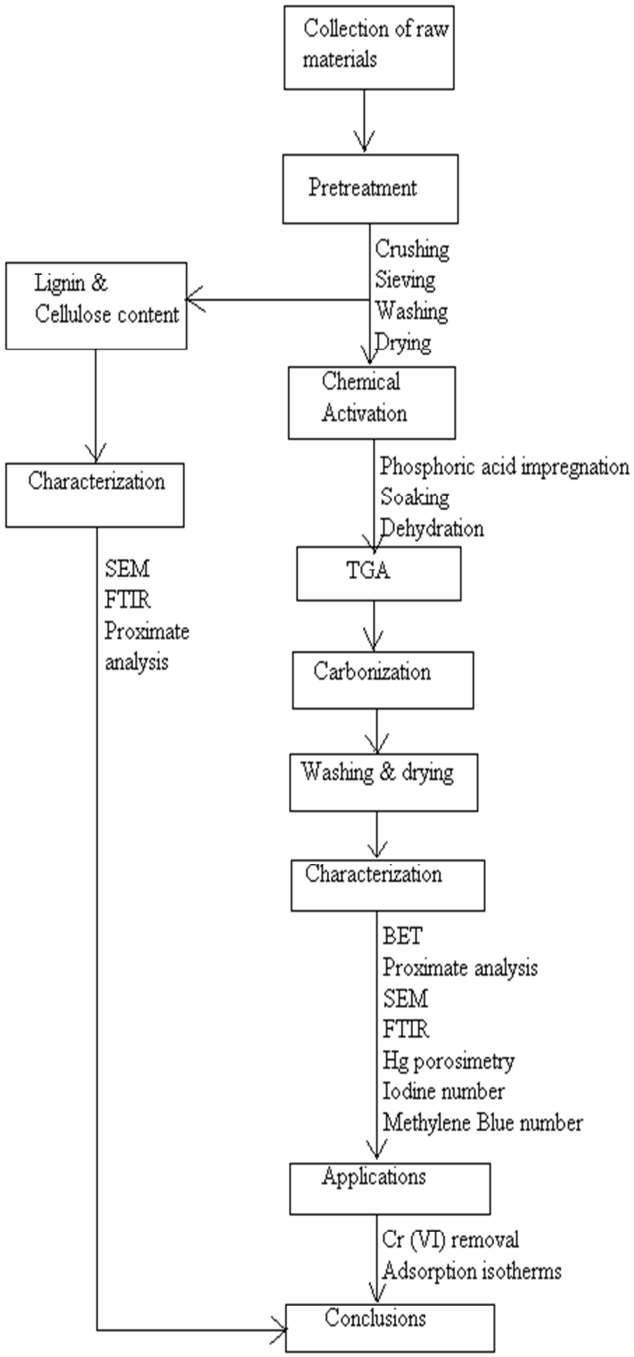

Fig. 1- Methodology of the project

3.1 Chemicals

The various chemicals used during the course of the project were phosphoric acid (88%), sulphuric acid (98%), acetone, 1, 5-diphenylcarbazide, potassium dichromate, sodium hydroxide, methylene blue dye, acetic acid, hydrochloric acid, sodium thiosulphate, iodine, starch, potassium iodide, potassium iodate, sodium carbonate, potassium permanganate etc. These all chemicals were bought from Merck India.

3.2 Instrumentation

The adsorption experiments were carried out in a shaker (Lab Companion model SI-300R). Scanning electron microscope (SEM-JEOL, JSM 6480 LV) was used to visualize the surface texture of the precursor and the prepared activated carbon sample. Fourier Transform Infrared spectrometry (Perkin Elmer, revolution of 4 cm^{-1}) was used to determine the organic functional groups present in the adsorbent. Tube furnace (OKAY 1400 ^{0}C electrical furnace, 40T 4Y) was used for the carbonization of the samples. Thermo-gravimetric Analyzer (Schimadzu, DTG-60H) was used to determine the weight loss of the chemically treated sample with rise in temperature. Specific surface area was determined using BET apparatus (Autosorb, Blue star Ltd.). Porosity and pore volumes were determined using mercury porosimetry (Quantachrome Poremaster 32). pH meter (Eutech instruments, pH 510) was used to adjust the pH of the solutions. Hot air oven was used for the drying of the samples as and when required. Absorbance readings were taken using UV spectrophotometer (Jasco V-530).

3.3 Raw materials

The raw materials used for the synthesis of activated carbon were coconut shell and bael fruit shell. The raw materials were collected from the environment.

3.4 Pretreatment of raw materials

The coconut shells and the bael fruit shells were initially sundried to remove moisture. Then the shells were crushed using a hand crusher to a particular size range. The crushed particles were sieved using a sieve shaker to obtain particles in the size range of 1.7-2 mm. These particles were then washed with water and dried in the hot air oven. After complete drying, the raw materials were ready for chemical activation.

3.5 Lignin and cellulose content

Lignin and cellulose content of coconut shell was taken from literature and was determined for bael fruit shell.

Lignin content determination was done using kappa number method. The kappa number is defined as the volume of 0.02 M potassium permanganate solution consumed by one gram of moisture-free pulp in an acidic medium [37].

0.1 g biomass was added to a mixture of 5 ml 0.02 M potassium permanganate solution and 20 ml 2 M sulphuric acid and mixed well for 10 minutes. Solid sample was separated from the solution by filtration. The filtrate was measured using UV spectrophotometer at 546 nm. The kappa number κ was calculated using the formula:

$$\kappa = (a/w)\ (A_0 - A_c)/A_0$$

a=volume of $KMnO_4$ used in the solution

w=weight of moisture free sample

A_0=spectral intensity at time t=0

A_c=spectral intensity at the end of the reaction

Accordingly, lignin content was determined using the formula

Lignin (wt %) =0.15κ……. [38]

Cellulose content was determined using semi-micro method of Updegraff [39]. A known amount of sample was taken in a glass centrifuge and mixed with 3 ml acetic/nitric reagent (150 ml 80% acetic acid + 15 ml conc. Nitric acid). It was placed in a boiling water bath for 30 min. with marbles on the top to reduce evaporation. Sample was centrifuged at 4000 rpm for 10 min and the supernatant liquid was discarded. It was washed with 10 ml distilled water by well mixing, centrifuging and discarding the supernatant liquid. 10 ml 67% sulphuric acid (v/v) was added, well mixed and allowed to stand for 1 hour. The solution was diluted with 100 ml distilled water and allowed to settle for 1 hour. 1 ml solution was transferred from the top to a test tube and 4 ml distilled water was added to it. The test tube was placed in an ice bath and 10 ml cold Anthrone reagent was added to it. The tube was placed in a boiling water bath for 16 min. The contents were cooled to room temperature. The absorbance of the solution was taken at 620 nm.

$$\text{Cellulose \%} = (Q_c\ D/W)\ 100$$

Q_c= Quantity of cellulose in mg from standard curve

D=Dilution test factor

W=Weight of sample taken

3.6 Chemical activation

The raw materials were mixed in the desired ratio and put in a beaker. 30% phosphoric acid was added to the precursor so as to completely wet all the particles in the acid solution. This was achieved by adding 1 ml acid per gram of the sample (i.e. for 20 gm precursor, 20 ml acid was added). The samples were allowed to remain soaked in the acid for 12 hours after which the beaker was put in the hot air oven till the acid was completely dehydrated to give dried black granular structures. This process required 24 - 48 hours depending on the amount of sample being prepared.

3.7 Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis measures the loss in weight of a material with respect to temperature and time. The analysis can be done in an atmosphere of air or nitrogen as per requirement. The analyzer is fitted with sensors which gives the weight of the sample at various times. It helps to determine an approximate working range of temperature for activation process. The parameters required for analysis are heating rate, maximum temperature, and holding time. A small amount (5mg approximately) of the chemically activated sample was taken in a vial and placed in the TGA analyzer. N_2 atmosphere was provided using a N_2 generator. The heating rate and maximum temperature were set as 10 ^{0}C/ min. and 800 ^{0}C respectively.

3.8 Carbonization

The impregnated samples were placed in a tube furnace (shown in the figure) and the temperature was set at 450 ^{0}C. The heating rate was adjusted at 4 ^{0}C/min. Inert atmosphere was provided by supplying N_2 gas using a N_2 generator. The N_2 flow rate was adjusted at 350 ml/min using a rotameter. The sample was allowed to remain at the desired temperature for 1 hour after which it was left to cool to room temperature. The activation temperature and time was changed as and when required. The samples were then taken out, washed with water till

the pH of the wash liquor was 6-7. After thorough washing the samples were dried in the hot air oven at 105^{0}C to give the final activated carbon.

Fig. 2- Tube furnace used for carbonization

3.9 Proximate analysis

ASTM defines proximate analysis as the determination by prescribed methods of moisture, volatile matter, fixed carbon, and ash. It is defined by ASTM D 121. The proximate analysis of the raw sample and the activated carbon were done using the following procedure [40].

3.9.1 Moisture content

A small amount of the sample was put in a crucible, covered with a lid and weighed using a weighing balance. The crucible was placed in the hot air oven at 150 ^{0}C with its lid removed and dried for 3 hours. The crucible was taken out, immediately covered with the lid, cooled in a dessicator and weighed.

The moisture content M = 100(B-F)/ (B-G)

B= Mass of crucible with lid + original sample

F= Mass of crucible with lid + dried sample

G= Mass of crucible with lid

3.9.2 Ash content

The crucible was ignited in the muffle furnace at 650 $\pm$ 25 ^{0}C for 1 hour. The crucible was placed in the dessicator, cooled to room temperature and weighed. A known amount of the sample which was dried in the hot air oven at 150 ^{0}C for 3 hours was put in the crucible and the crucible was placed back in the muffle furnace at 650 $\pm$ 25 ^{0}C for 3 hours. The crucible was taken out of the furnace, placed in the dessicator, cooled to room temperature and weighed.

The ash content A= 100(F-G)/ (B-G)

G= Mass of empty crucible

B=Mass of crucible + dried sample

F=Mass of crucible + ashed sample

3.9.3 Volatile matter content

A known amount of sample was put in a crucible. The crucible was placed in a muffle furnace at 900 ^{0}C $\pm$ 10 ^{0}C, covered with lid, and placed for exactly 7 minutes. The crucible was taken out, allowed to cool and weighed.

Volatile matter on dry basis VM=100[100(B-F)-M (B-G)]/ [(B-G) (100-M)]

B= Mass of crucible, lid and sample before heating

F= Mass of crucible, lid and contents after heating

G= Mass of empty crucible and lid

M= % of moisture as determined above

3.9.4 Fixed carbon content

Fixed carbon FC=100-(volatile matter + ash content)

3.10 Scanning Electron Microscope (SEM)

Scanning electron microscope is a type of microscope which uses a beam of highly energetic electrons to scan a sample and produce its image. It consists of an electron gun which acts as a source for electrons. The electron beam is focused by a pair of condenser lenses made of magnets which are capable of bending the path of electrons. Sample to be analyzed is placed in the sample chamber. The electron beam strikes the sample, gets decelerated, and produces a variety of signals like secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light and heat. The secondary electrons are picked up by the detectors and produce images of the object's surface on the monitor. The entire operation takes place inside a vacuum chamber.

The precursor and activated carbon samples were analyzed in a SEM to visualize the porous structure. The magnification was adjusted so as to get a clear picture.

3.11 BET

BET stands for Brunauer, Emmett and Teller-the men who proposed a theory to measure the surface area of solid particles like porous powders. The basic principle involved is the adsorption of gas molecules to the surface of the solid whose surface area is required. From the area of each molecule, the whole area of the solid can be calculated.

BET theory is based on multilayer adsorption with the following assumptions [41]:

- Gas molecules can be physically adsorbed on the solid surface and form infinite layers
- There is no interaction between the layers
- Langmuir theory is applied to each layer

The BET equation is given by:

$1/v\ [(P_0/P)-1] = (c-1)\ (P/P_0)/\ (v_m c) + 1/\ (v_m c)$

P_0= Saturation pressure of the adsorbate

P= Equilibrium pressure of the adsorbate

v= Volume of gas adsorbed

v_m= Volume of gas adsorbed in the monolayer

c= BET constant given by $\exp (E_1-E_L)/RT$

E_1= Heat of adsorption for the first layer

E_L= Heat of adsorption for higher layers

A plot of $1/v\ [(P_0/P)-1]$ v/s (P/P_0) is obtained from the BET analysis. From the slope and intercept of the line, v_m and c are obtained. Surface area S of the solid sample is given by

$$S= (v_m N s)/ (VX)$$

N= Avogadro's number

s= adsorption cross-section of the gas being adsorbed

V= molar volume of the gas being adsorbed

X= mass of the adsorbent

A small amount of the sample was taken in the tube and the tube was placed in a dewar containing liquid nitrogen. Initially the sample was degasified to remove the impurities and gases. Then gaseous nitrogen was passed through the sample and based on adsorption of the gas, the surface area of the sample was calculated.

3.12 Fourier Transform Infra-Red spectroscopy (FTIR)

In FTIR, infrared radiation is passed through the sample. A part of this radiation is absorbed by the sample and the other part is transmitted. This produces a spectrum in the form of transmittance/absorbance plotted against the wave number. This spectrum represents a fingerprint of the sample with absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms which make up the material. Thus, it gives an idea about the organic functional groups present in the sample.

Two pellets were prepared-one of pure KBr and the other of the sample mixed with KBr. The concentration of sample in KBr was between 0.2-1 %. The KBr pellet was used as reference in the FTIR. Then the sample pellet was placed in the device to obtain the IR spectrum in terms of transmittance v/s wave number plot.

3.13 Mercury porosimetry

Mercury porosimetry is an effective tool for the measurement of porosity and pore volume of porous substances. Initially gas, moisture and other impurities are evacuated from the sample and vacuum is created. Mercury is transferred into the sample under vacuum and gradually

the pressure is increased. Amount of mercury intruded is measured continuously as a function of applied pressure. Further analysis gives an intrusion extrusion curve and parameters describing the pore structure are calculated from the data.

The sample was placed in the vacuum chamber and the procedure as mentioned above was applied to measure the desired parameters.

3.14 pH

pH was determined using the standard method ASTMD3838-80. 1 g activated carbon sample was put in a conical flask and 100 ml distilled water was added to it. The mixture was stirred for 1 hour. pH readings were taken using pH meter.

3.15 Iodine number

Iodine number is the milligrams of iodine adsorbed by 1 gram of activated carbon from a standard 0.1 N iodine solution when the equilibrium iodine concentration is exactly 0.02 N. iodine number is a measure of the micropore content of the activated carbon. A higher iodine number indicates higher microporosity of the sample.

ASTM D4607 – 94(2006) gives the standard procedure for the determination of the iodine number of the activated carbon. 0.7-2g of dried activated carbon was mixed with 10 ml of 5% by weight HCl and swirled in a conical flask until the activated carbon was wetted. The flask was boiled for 30 sec. by placing it on a hot plate. The contents of the flask wre cooled to room temperature and 100 ml 0.1N iodine solution was added to it. The flask was shaken vigorously for 30 sec. The contents were filtered through a filter paper. Initial 20-30 ml of the filtrate was discarded and the remaining filtrate was collected in a clean beaker. 50 ml of this filtrate was titrated against 0.1N sodium thiosulphate solution until yellow color just disappeared. 1 ml starch solution was added and titration was continued till blue color just

disappeared. Concentration of the resulting solution was calculated and if the equilibrium concentration was not within 0.008 to 0.0334, the procedure was repeated with a different amount of activated carbon [40].

3.16 Methylene blue number

Methylene blue number is defined as the milligrams of methylene blue dye adsorbed by 1g of dried activated carbon. It is a measure of the mesopore content of the activated carbon.

1200 mg/l methylene blue stock solution was prepared. The sample was diluted to give solutions of 5 different concentrations. A standard calibration curve was prepared by measuring the absorbance at 665 nm. A known concentration solution was prepared from the stock solution and a known amount of activated carbon was put into it. The flask was placed in a shaker at 25 ^{0}C for 24 hours at 110 rpm. The absorbance of the resulting solution was measured at 665 nm and the concentration was calculated from the calibration plot. The methylene blue number was calculated as

$q_e = V (C_0 - C_e)/X$

q_e= Amount of MB adsorbed

C_0= Initial concentration

C_e= Equilibrium concentration

X= Amount of adsorbent

3.17 Adsorption studies

The prepared activated carbon sample was used to study the adsorption kinetics of Cr (VI) ions in water. Stock chromium solution was prepared by dissolving 141.4 mg potassium dichromate in 1000 ml distilled water. Diphenylcarbazide solution was prepared by

dissolving 250 mg 1, 5-diphenylcarbazide in 50 ml acetone and was used as an indicator for Cr (VI) ions. Addition of diphenylcarbazide to a solution containing Cr (VI) ions gave pink color. A calibration plot was prepared for the Cr (VI) solution of pH 1. The absorbance readings were taken at 540 nm. The effect of contact time, pH, adsorbent dosage, temperature and initial concentration on the removal of Cr (VI) from water using activated carbon was studied. Adsorption isotherms using Langmuir, Freundlich and Temkin models were developed.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.RESULTS AND DISCUSSIONS

4.1 Lignin and cellulose content

The lignin and cellulose contents of coconut shell, bael fruit shell and a mixture of bael fruit shell particles to coconut shell particles in 1:2 ratio are given below.

Table 4: Lignin and cellulose content of precursor

	Coconut shell particles [42]	Bael fruit shell particles	Mixture (bael:coconut::1:2)
Lignin (%)	30.1	19.9	26.1
Cellulose (%)	19.8	24.4	20.7

As can be seen from the table, coconut shell particles have higher lignin content and lower cellulose content compared to bael fruit shell particles. The mixture of the two has a considerably lower lignin content compared to that of coconut shell particles. Thus it is likely to produce activated carbon with higher microporosity compared to that of coconut shell based activated carbon [24] and provides a basis for further study.

4.2 Thermo-Gravimetric analysis (TGA)

The TGA result of the chemically treated precursor is shown below. As seen from the plot, there is a drastic change in the weight of the sample after the temperature reaches 400 ^{0}C and it continues till temperature attains nearly 600 ^{0}C. During this temperature range, the sample loses bulk of its volatile matter and moisture. The constant line in the plot seen after 3500 sec depicts the ash that is left over from the sample.

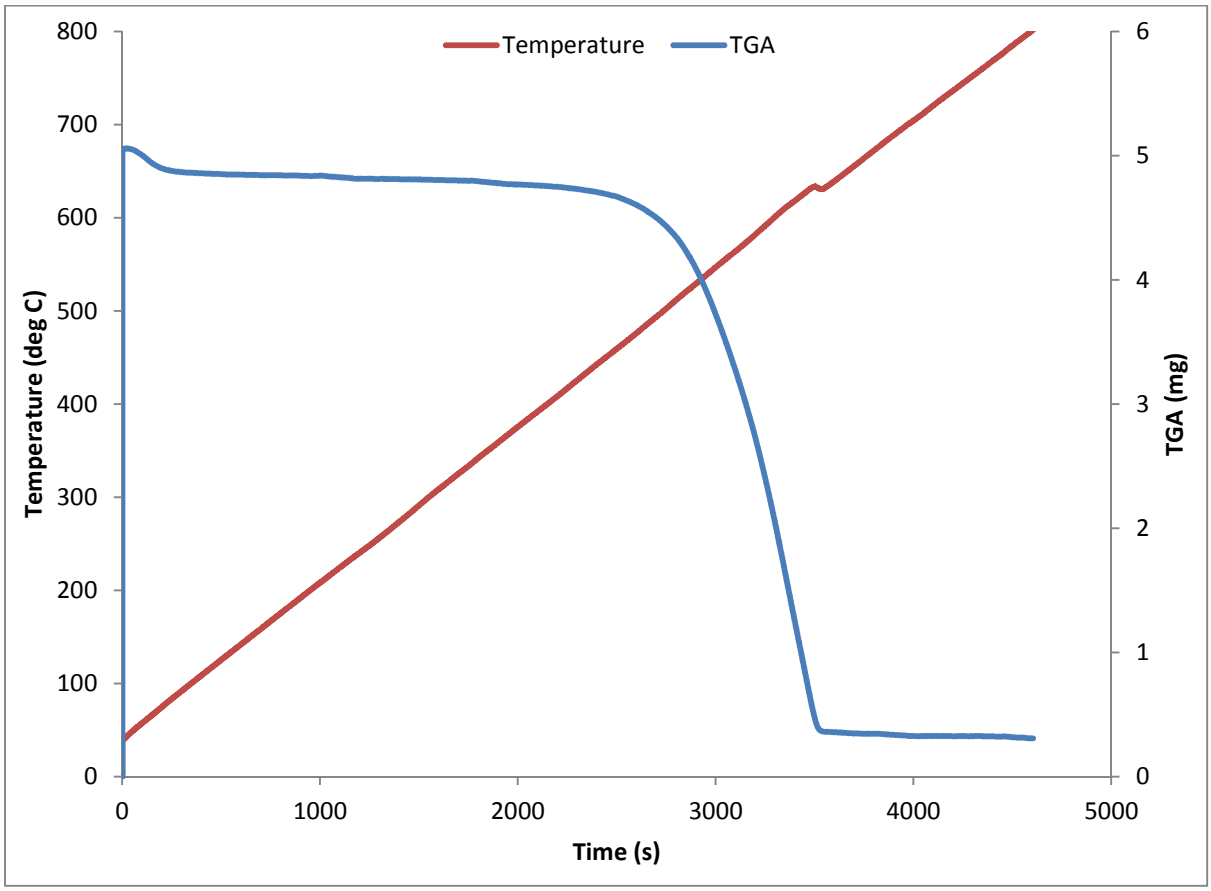

Fig. 3-TGA thermograph of the chemically treated precursor

4.3 Proximate analysis

The following table shows the proximate analysis of the precursor consisting of a mixture of bael fruit shell particles to coconut particles in 1:2 ratio and the activated carbon sample prepared from it.

Table 5: Proximate analysis of precursor and activated carbon

Parameters	**Raw sample (Bael:Coconut::1:2)**	**Activated carbon**
Moisture (%)	10.33	16.72
Volatile matter (%)	79.65	22.51
Fixed carbon (%)	19.74	76.71
Ash (%)	0.61	0.78

As can be seen from the table, the precursor had a higher volatile matter content and lower fixed carbon content. When the sample was heated at high temperature, most part of the volatile matter was lost from the sample and this led to increase in fixed carbon content of the activated carbon. The increase in moisture content could have been due to washing involved while preparation of the activated carbon. The ash content of the activated carbon was found to be quite low which is quite desirable as it tends to reduce the overall activity of the activated carbon. The increase in ash content in the activated carbon sample can be attributed to addition of phosphoric acid to the precursor during chemical activation which might have led to increase in the inorganic content of the sample.

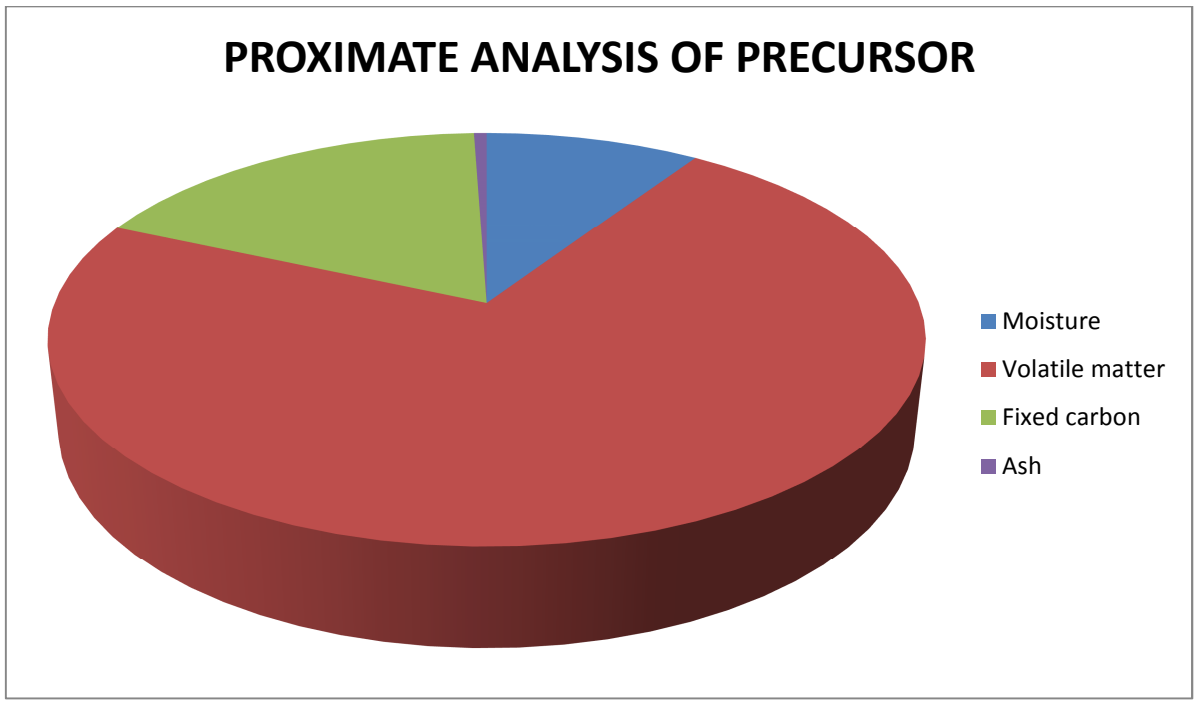

Fig. 4- Proximate analysis of precursor

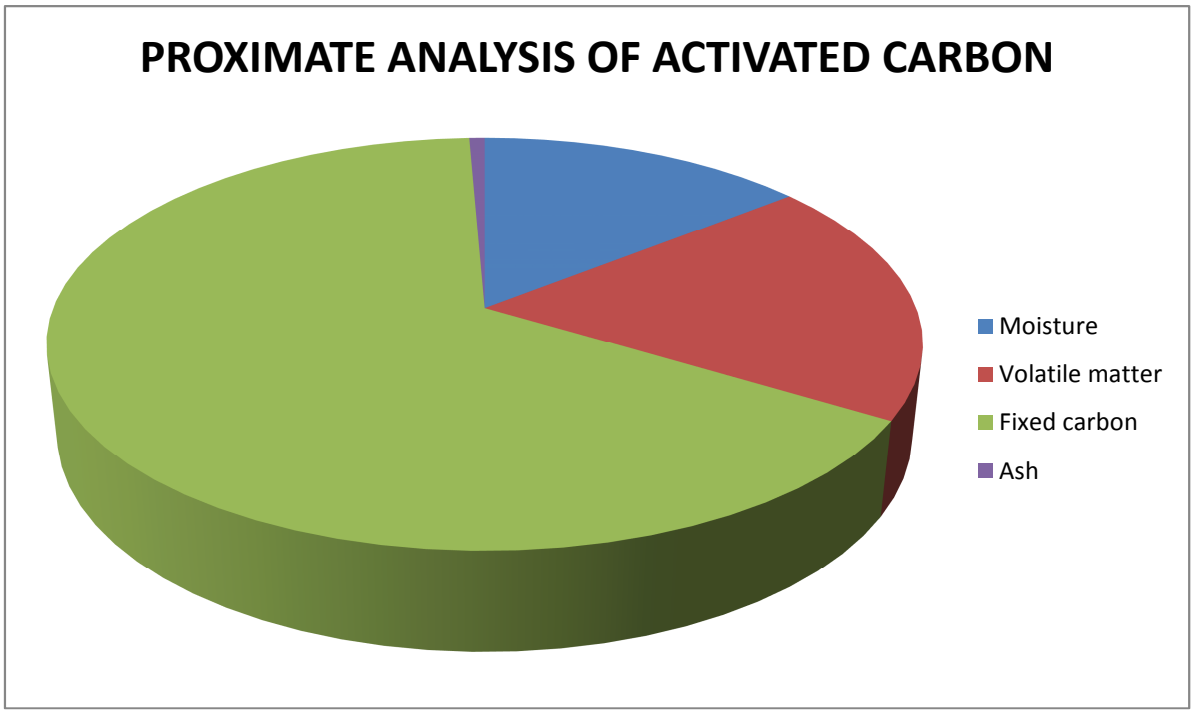

Fig. 5- Proximate analysis of activated carbon

4.4 Scanning Electron Microscope (SEM)

Scanning electron microscope images were taken to observe the surface topography of the sample. Basically, the pore structures of the raw samples and activated carbons were observed. The micrographs of the precursor and activated carbon prepared from it are shown below.

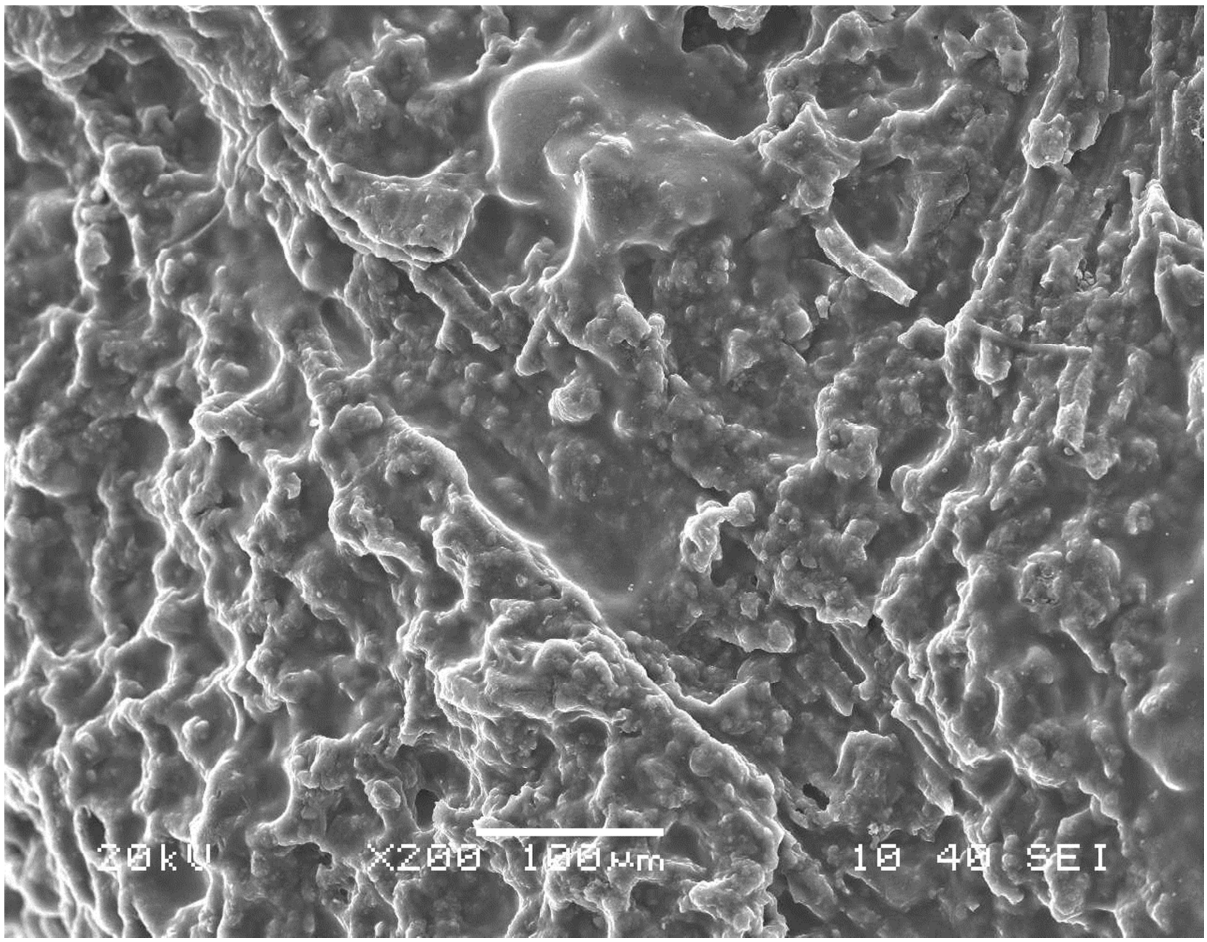

Fig. 6 - SEM image of the precursor (Bael:Coconut::1:2)

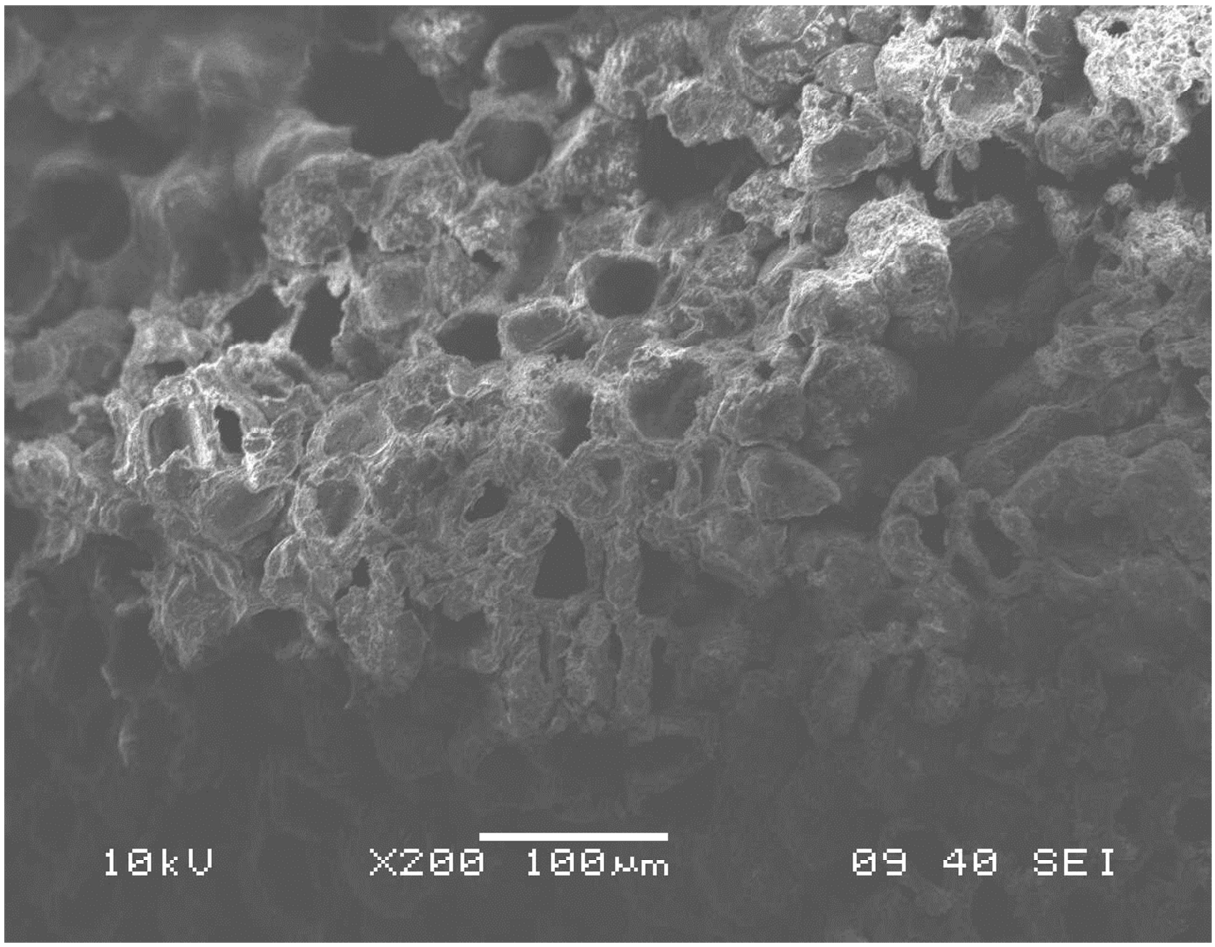

Fig. 7 - SEM image of the activated carbon

As can be seen from the two images, there is hardly any pore visible in the precursor while the pores are distinctly visible in the activated carbon. This supports the fact that the activated carbon has a highly developed porous structure.

4.5 BET

The BET surface area is one of the parameters that determine the absorption capacity of the activated carbon. Higher surface area implies more availability of surface for adsorption hence better adsorption capacity.

The precursor under study being a mixture of coconut shell and bael fruit shell, the BET surface areas of coconut shell and bael fruit shell based activated carbons were determined first and they are shown below.

Table 6: BET surface area of activated carbon derived from coconut and bael fruit shell

Precursor for activated carbon	**BET surface area (m^2/g)**
Coconut shell	1008.96
Bael fruit shell	1427.12

Results show that bael fruit shell based activated carbons have a higher BET surface area than those derived from coconut shell. Thus an activated carbon derived by mixing the two raw materials was expected to show higher surface area than that of coconut shell based activated carbon.

The BET surface area of the activated carbon prepared by mixing coconut shell and bael fruit shell in different ratios are shown below.

Table 7: Specific surface area of activated carbon derived from a mixture of coconut and bael fruit shell in different ratios

Precursor	**BET surface area (m^2/g)**
Bael:Coconut::1:1	1364.84
Bael:Coconut::1:2	1352.32
Bael:Coconut::1:3	1024.16

Bael:Coconut::1:1 ratio had the highest BET surface area of 1364.84 m^2/g. All the three samples had surface areas between coconut shell and bael fruit shell based activated carbons.

The highest surface area obtained (i.e. 1364.84 m^2/g) was around 35% more than coconut shell based activated carbon.

There was hardly any difference in the surface areas of Bael:Coconut::1:1 and Bael:Coconut::1:2. Availability of bael fruit shell in the environment is a matter of concern. Bael:coconut::1:1 requires highest amount of bael fruit shell. Even though bael:coconut::1:3 requires lowest amount of bael fruit shell, the BET surface area is quite low. Thus, activated carbon derived from bael:coconut::1:2 ratio was selected for further analysis.

The effect of acid concentration on the BET surface area was studied. 3 different concentrations of phosphoric acid (20%, 30%, and 40%) were used to chemically activate the precursor. The following figure shows the effect of concentration on the BET surface area.

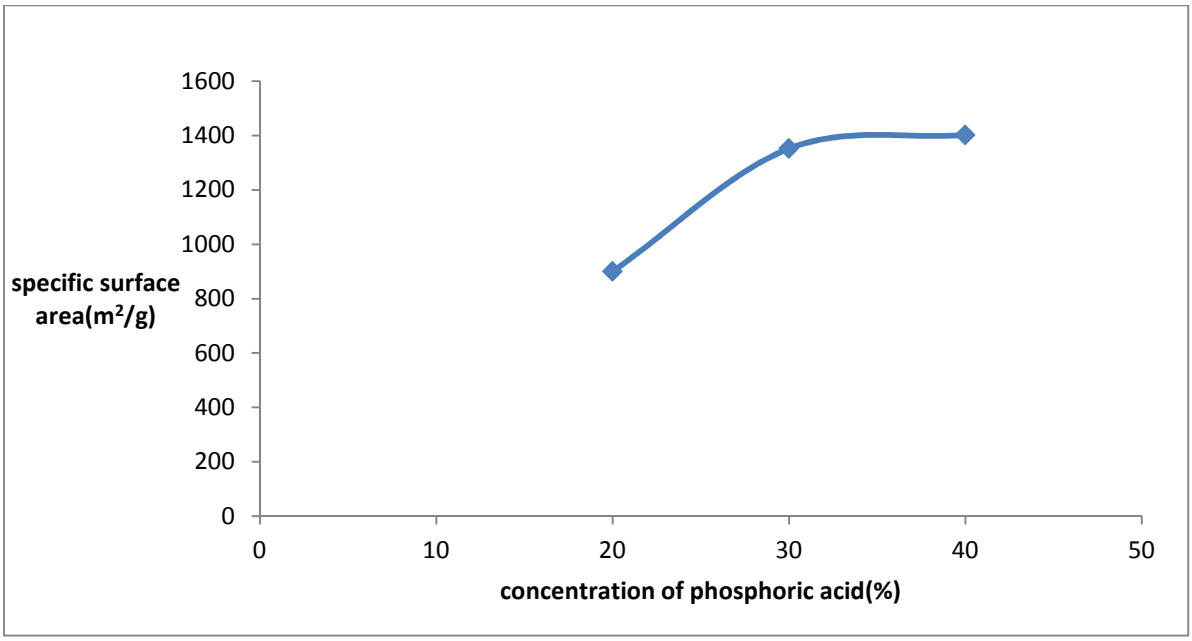

Fig.8- Specific surface area v/s Concentration of phosphoric acid

The BET surface area increased vastly due to increase in concentration from 20% to 30 % but further increase in concentration showed hardly any increase in surface area.

4.6 Yield

Yield of the activated carbon was studied by varying the concentration of phosphoric acid and the activation temperature.

The effect of variation in concentration of phosphoric acid on the yield of the activated carbon is shown below:

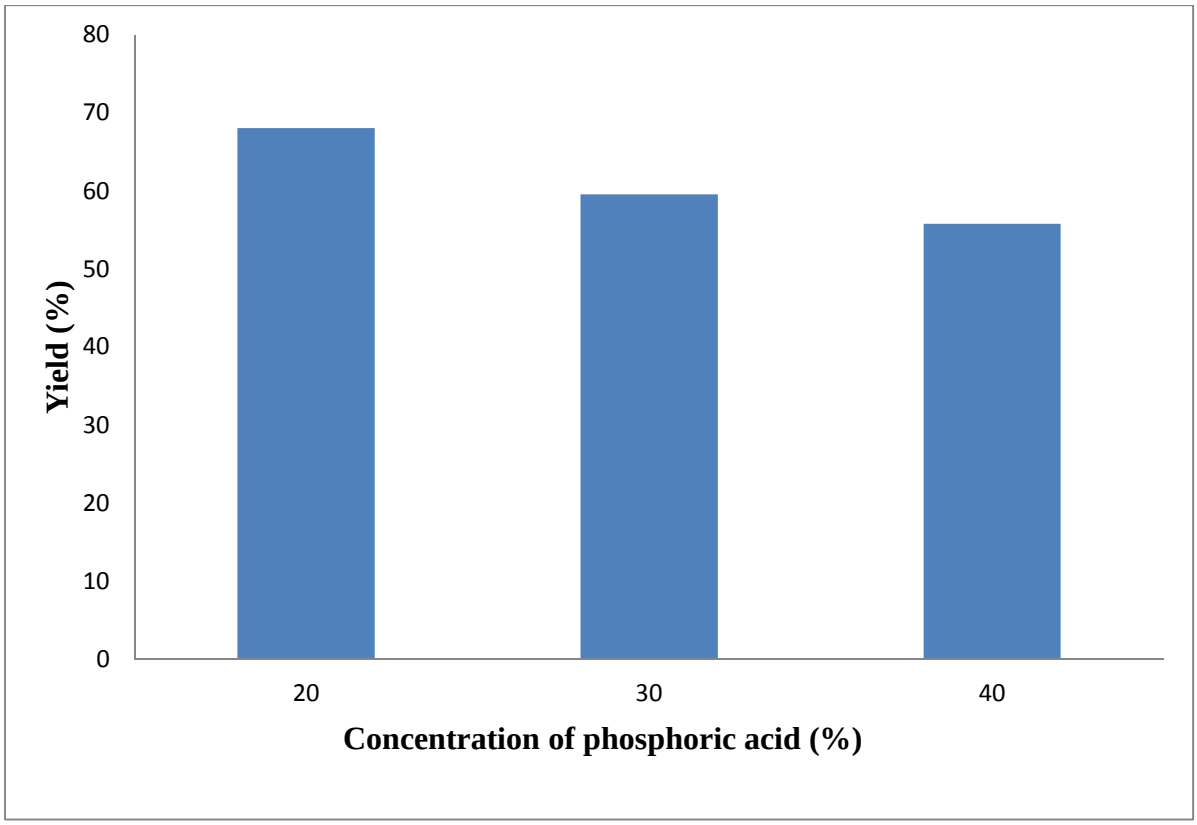

Fig. 9- Yield of activated carbon at different concentration of phosphoric acids

The yield was found to decrease with increase in concentration of phosphoric acid.

Phosphoric acid tends to produce dehydrating effect on cellulose, hemicellulose and lignin in the interior of the particles during heat treatment [43]. The acid tends to break the ligno-cellulosic bonds of the precursors and release the non-carbon elements in terms of liquids (tars) and gases leaving behind a rigid carbon skeleton [44]. More and more degradation

occurs with increase in concentration of the phosphoric acid thus leading to more evolution of liquid and gaseous products and consequently lower yield.

The effect of activation temperature on the yield is shown below

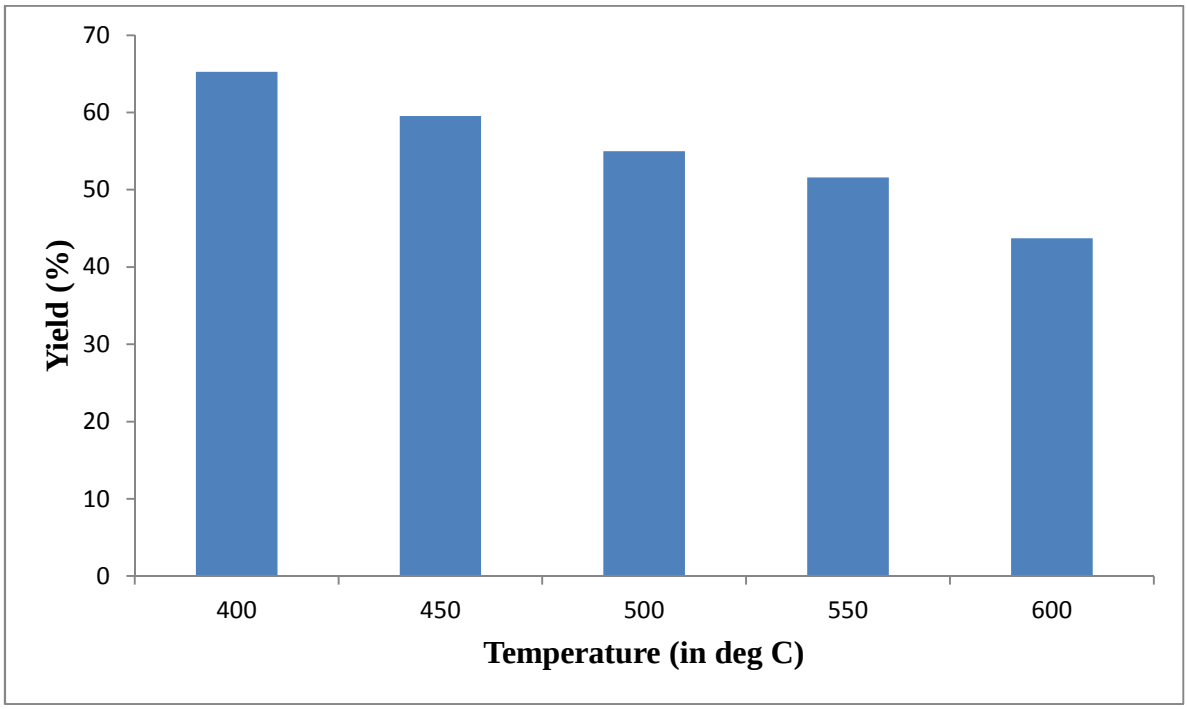

Fig. 10- Effect of activation temperature on yield of activated carbon

Higher temperature facilitates more and more removal of volatiles from the activated carbon thus resulting in lower yield

4.7 Fourier Transform Infra-Red spectroscopy (FTIR)

The transmittance spectra of the activated carbon obtained through FTIR analysis is shown below. Peaks corresponding to 3602, 3506 and 3452 cm^{-1} indicated the presence of monomeric alcohols, phenols and amines. Presence of alkenes is confirmed from the presence of peaks at 1658 and 3000 cm^{-1}. Presence of a peak at 2888 cm^{-1} confirms the presence of alkanes. Aldehydes, ketones, carboxylic acids and esters are confirmed by the presence of

peaks at 1718 and 1776 cm^{-1}. Also the peak at 1510 cm^{-1} confirmed the presence of benzene ring. Peaks at 2336 and 2406 cm^{-1} indicated the presence of alkynes and nitriles.

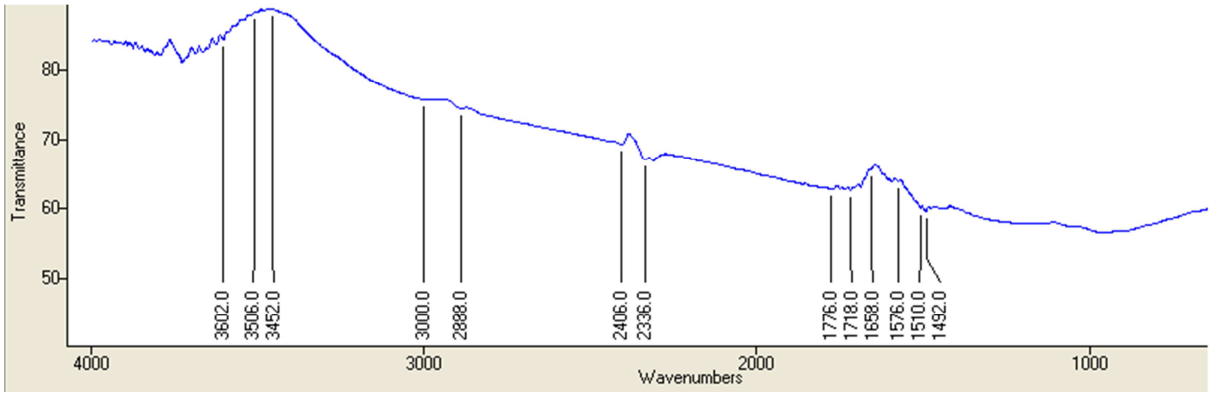

Fig. 11-FTIR spectra of activated carbon sample

4.8 Mercury porosimetry

Mercury porosimetry was done on the activated carbon samples prepared from coconut shell, bael fruit shell and the mixture of the two (Bael:Coconut::1:2) to measure the pore volume of the samples.

Table 8: - Pore volume of activated carbon derived from coconut, bael fruit and a mixture of coconut and bael

Precursor for activated carbon	**Pore volume (cc/g)**
Coconut	0.072
Bael fruit	0.1741
Bael:Coconut::1:2	0.1214

The activated carbon prepared from the mixture of coconut and bael fruit shell showed considerably higher pore volume (around 69%) compared to that of coconut shell based activated carbon.

4.9 pH

The standard test method for the determination of pH of activated carbon ASTMD3838-80 was used. The pH of the prepared sample was found to be 6.63.

4.10 Iodine number

Iodine number of the activated carbon was determined using standard ASTM method and was found to be 1234 mg/g. The iodine number of commercial coconut shell based activated carbon is 894 mg/g [45]. Iodine number is a measure of the microporosity of the activated carbon. Hence, the activated carbon syhthesized from the mixture of bael and coconut shells in 1:2 ratio has higher microporosity (nearly 38%) than commercial coconut shell based activated carbon.

4.11 Methylene blue number

The methylene blue number of the activated carbon was found to be 234 mg/g. The methylene blue number of activated carbon samples prepared from coconut shells has been found to be 212 mg/g [46]. Methylene blue number is a measure of the mesoporosity of the activated carbon. Hence, there is only 10% increase in the mesoporosity of the activated carbon synthesized from the mixture of bael and coconut shells in 1:2 ratio compared to that of activated carbon synthesized from coconut shells.

4.12 Batch adsorption studies

Batch adsorption studies were performed on removal of Cr (VI) ions using activated carbon. The effect of contact time, pH, adsorbent dosage, temperature and initial concentration of Cr (VI) ions were investigated.

The effect of contact time on removal efficiency is shown below.

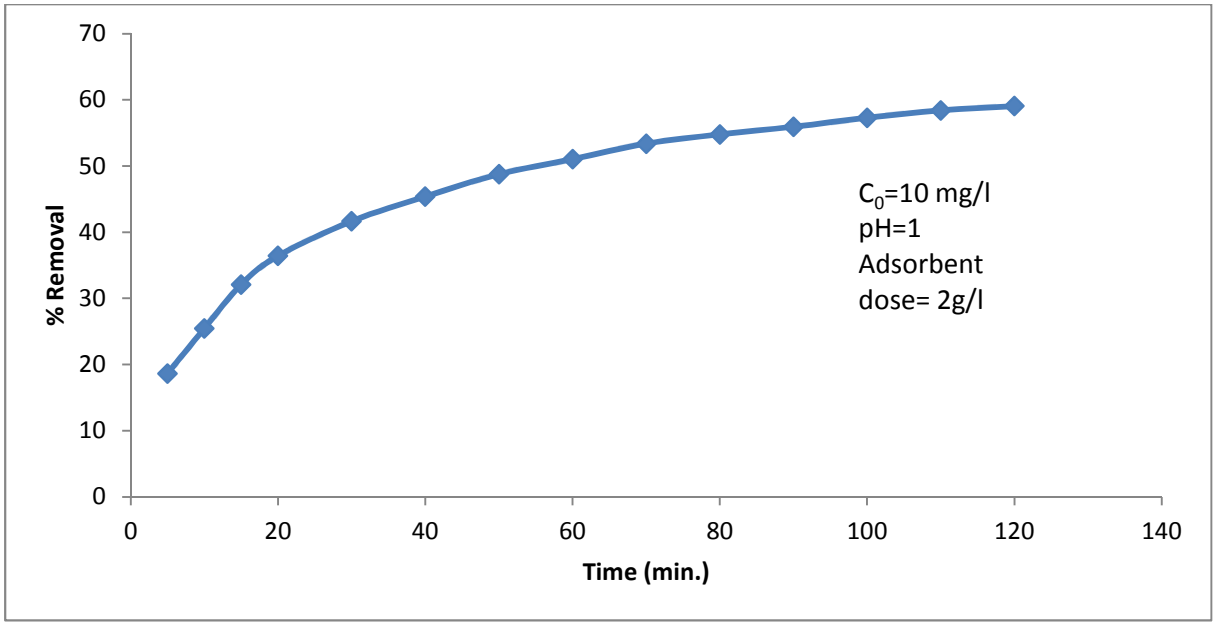

Fig. 12- Effect of contact time on removal of Cr (VI) ion

Initially the rate of removal is high owing to high concentration of Cr (VI) ions. As time progresses, the concentration of Cr (VI) ions decreases in the solution and increase on the surface of the adsorbent. Thus, the system tends to attain equilibrium.

The effect of pH on removal efficiency is shown below.

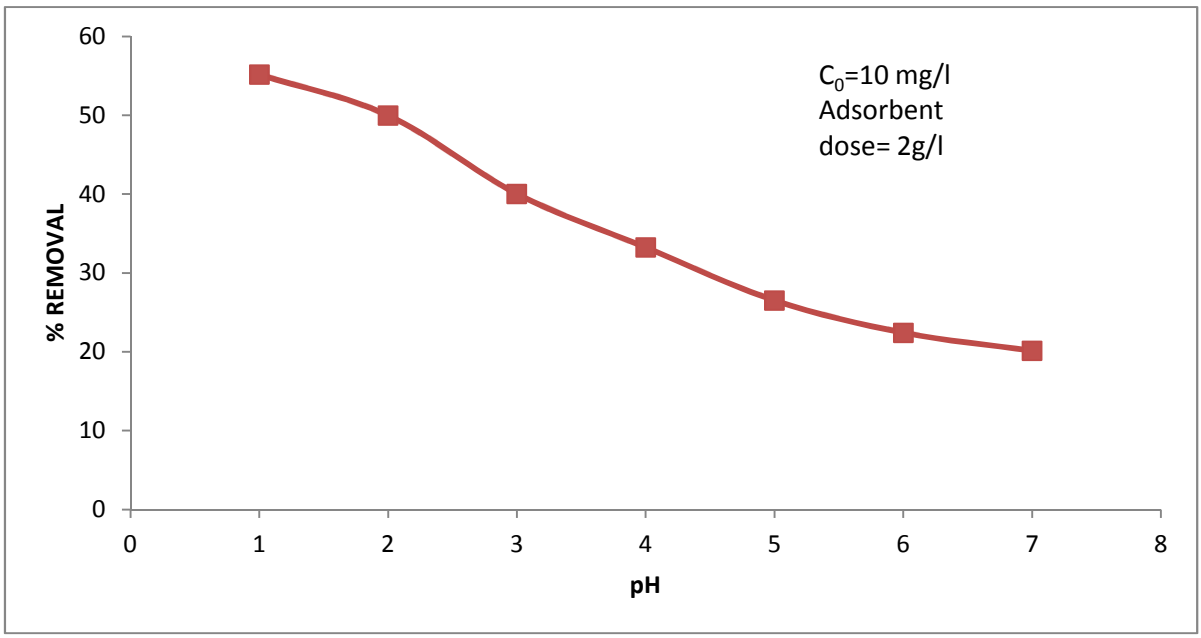

Fig. 13- Effect of pH on removal of Cr (VI) ion

At low pH values (< 3), the surface of activated carbons contain more positively charged functional groups and at pH values above 3 they contain more negatively charged functional groups [22]. Thus at low pH, the positively charged functional groups tend to attract he negatively charged dichromate ions thus facilitating the removal of Cr (VI) from water but at higher pH negatively charged surface functional groups tend to repel the negatively charged dichromate ions.

The effect of adsorbent dosage on removal efficiency is shown below.

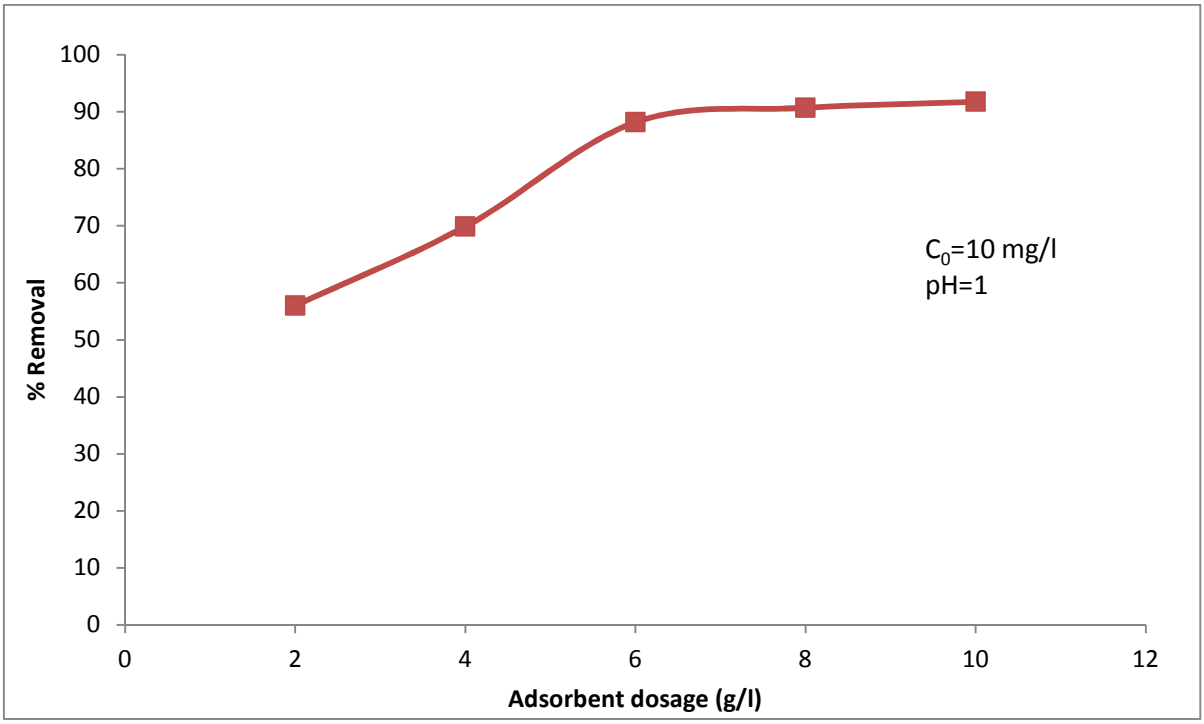

Fig. 14 - Effect of adsorbent dosage on removal of Cr (VI) ion

Initially as adsorbent dosage was increased, the percentage removal increased rapidly but beyond an adsorbent dosage of 6 g/l, the percentage removal became constant. This is because with increase in the amount of adsorbent, more and more Cr (VI) ions were removed which decreased the concentration of Cr (VI) ions in the solution which is the driving force for adsorption.

The effect of temperature on removal efficiency is shown below.

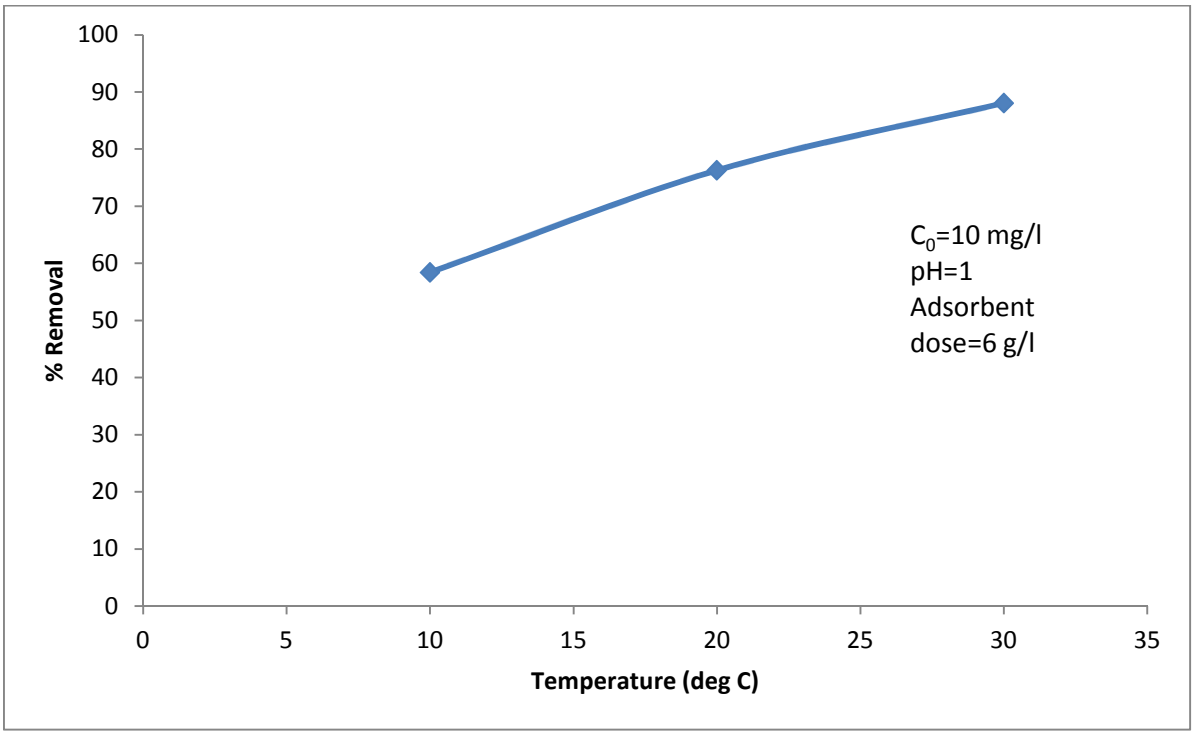

Fig. 15- Effect of temperature on removal of Cr (VI) ion

The percentage removal of Cr (VI) increased on increasing the temperature. This could be attributed to two factors- increased mobility of Cr (VI) ions and increased number of molecules acquiring the required energy to undergo interaction with the adsorption site [47].

The effect of initial concentration of Cr (VI) ion on removal efficiency is shown below.

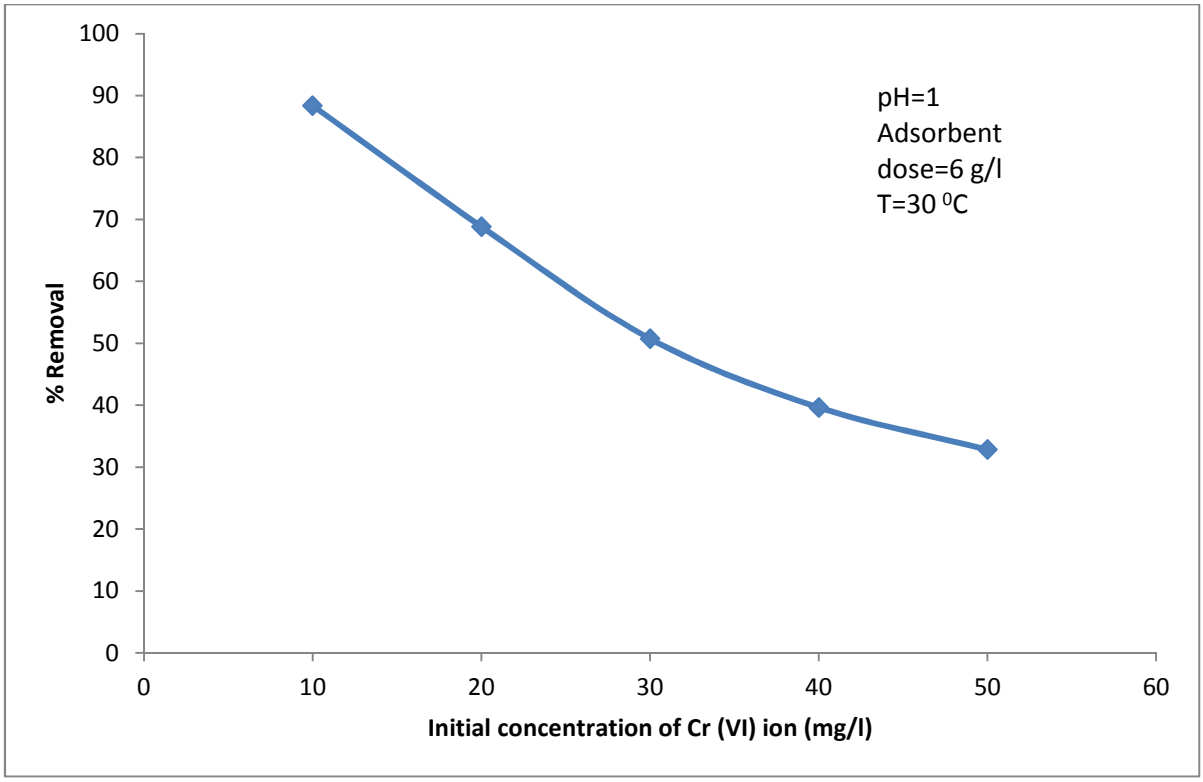

Fig. 16- Effect of initial concentration of Cr (VI) on removal of Cr (VI) ions

The percentage removal was found to decrease with increase in initial concentration of Cr (VI) ions.

4.13 Adsorption isotherms

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir, Freundlich and Temkin adsorption models. Each of the three models makes use of a parameter q_e (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium).

$q_e = (C_0 - C_e)V/X$

C_0=Initial concentration of solution

C_e=Equilibrium concentration of solution

V=Volume of solution

X=Amount of adsorbent used

4.13.1 Langmuir model [48]

The Langmuir isotherm model is given by

$$q_e=(q_m\, bC_e)/\ (1+bC_e)$$

q_m= Maximum amount of adsorbate adsorbed per unit mass of adsorbent

b= Langmuir constant

Langmuir modelwas fitted tothe experimental data as shown in the figure below

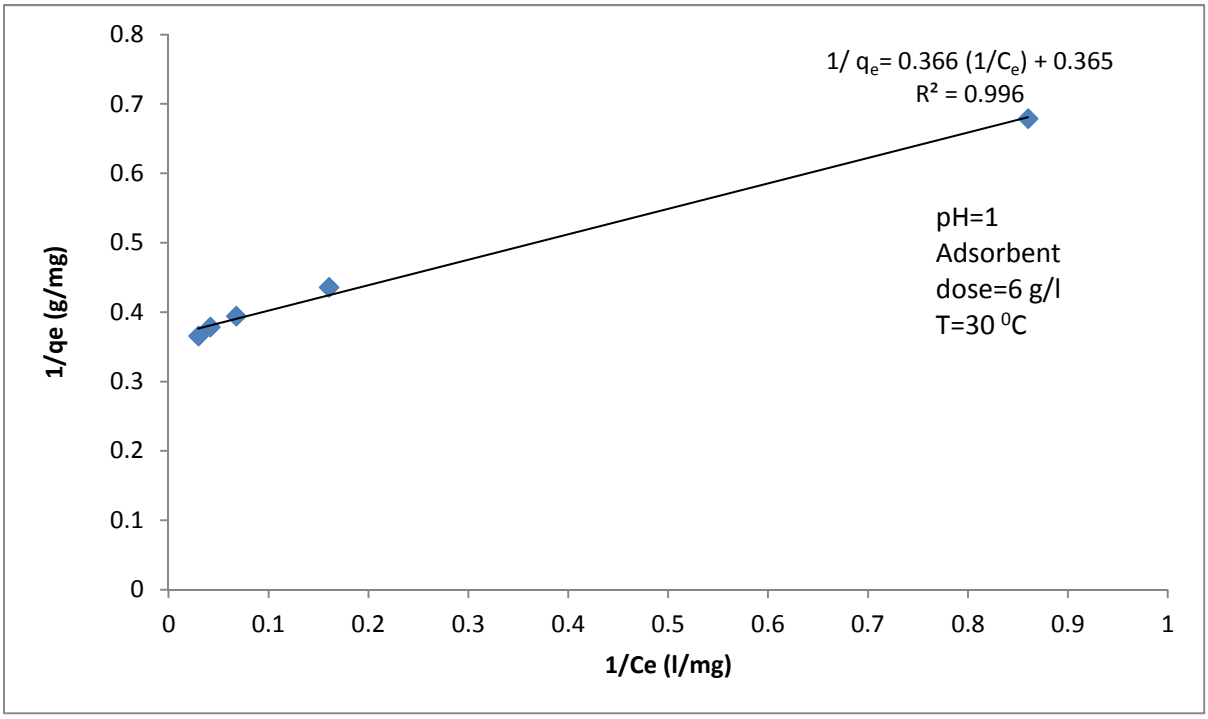

Fig. 17- Langmuir model

A seen from the figure, Langmuir model fits well to the experimental data with R^2=0.996. The values of q_m and b were determined to be 2.74 mg/g and 0.997 l/mg.

4.13.2 Freundlich model [49]

The Freundlich isotherm model is given by

$$q_e=k(C_e)^{1/n}$$

k= Freundlich constant

1/n = sorption intensity

Freundlich modelwas fitted tothe experimental data as shown in the figure below.

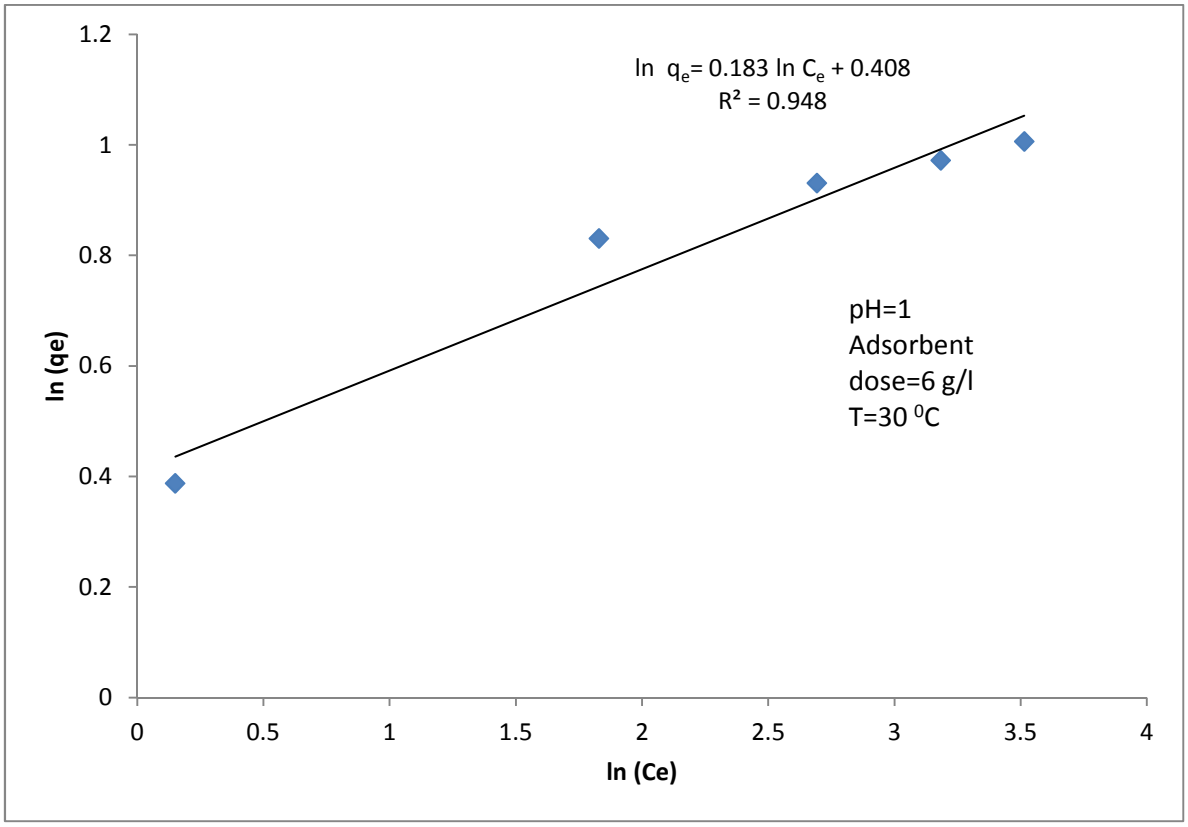

Fig. 18- Freundlich model

As seen from the figure the experimental data fits the Freundlich model with R^2=0.948. Freundlich constant k=1.504 and sorption intensity 1/n= 0.183. As the value of 1/n is less than 1, it indicates a favorable isotherm.

4.13.3 Temkin model [50]

The Temkinisotherm model is given by

$$q_e = (RT/b_T) \ln (K_T C_e)$$

T=Absolute temperature in K

R=Universal gas constant

K_T is the equilibrium binding constant

b_T is the variation of adsorption energy

Temkin model was fitted tothe experimental data as shown in the figure below.

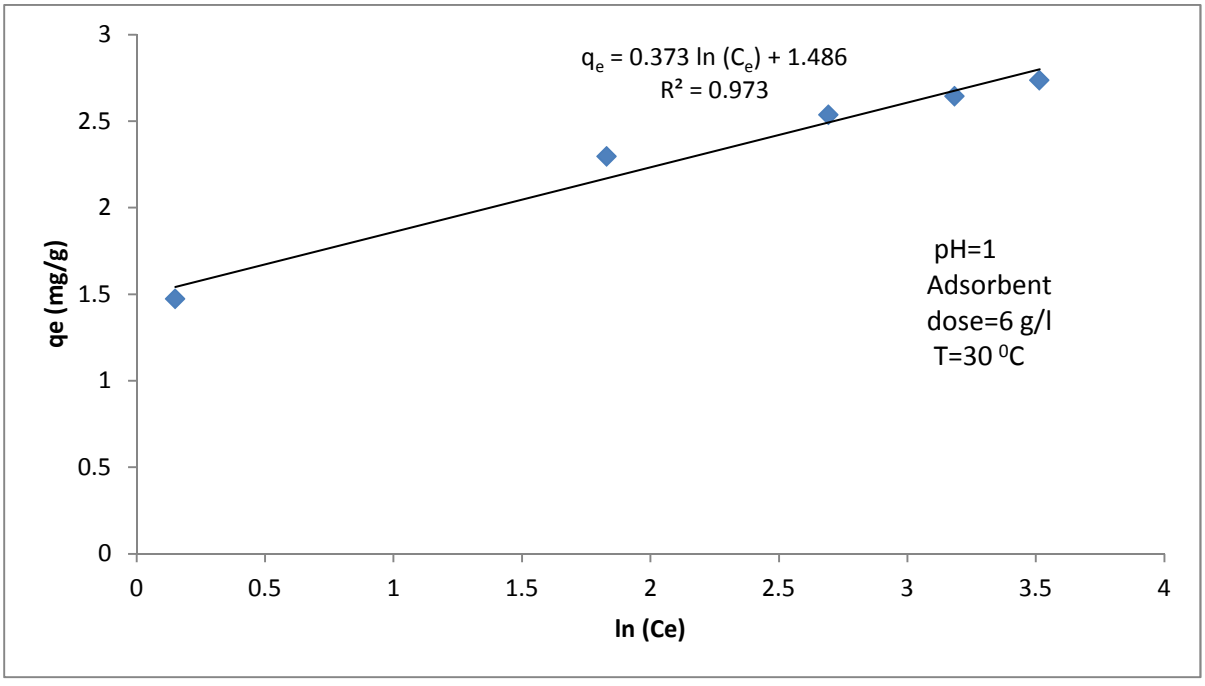

Fig. 19- Temkin model

As seen from the figure the experimental data fits the Temkin model with R^2=0.973.

Equilibrium binding constant K_T=53.73 l/mg and variation of adsorption energy b_T=6.754 kJ/mol.

The experimental data along with the three adsorption models have been shown below.

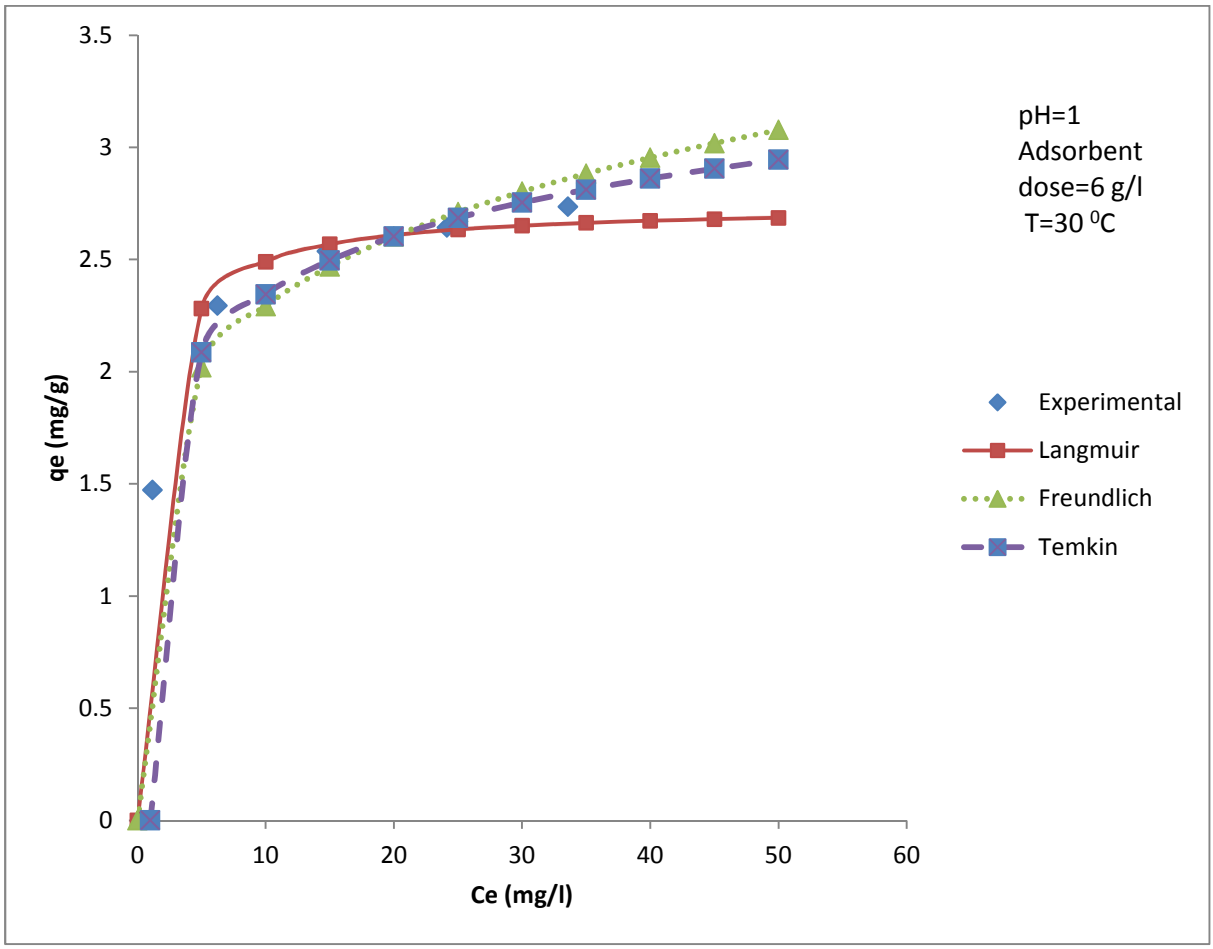

Fig. 20- Langmuir, Freundlich and Temkin isotherms for Cr (VI) removal

CHAPTER 5

CONCLUSIONS

5. CONCLUSIONS

A novel adsorbent was synthesized using a mixture of bael and coconut shell particles in 1:2 ratio. Characterization of the synthesized activated carbon was done with respect to its BET surface area, proximate analysis, SEM, FTIR, mercury porosimetry, pH, yield, iodine number and methylene blue number. The activated carbon was used to study the removal of Cr (VI) removal from water. The effect of contact time, pH, adsorbent dosage, temperature and initial concentration of Cr (VI) ions on the Cr (VI) removal efficiency of the activated carbon was studied and based on the experimental data, Langmuir, Freundlich and Temkin isotherm models were fitted. Based on the study, following conclusions were made.

- High surface area activated carbon was synthesized using bael and coconut shell particles. The surface area was found to be more than that of the coconut shell based activated carbon.
- The effect of acid concentration on the BET surface area was studied. 3 different concentrations of phosphoric acid (20%, 30%, and 40%) were used to impregnate the sample. The BET surface area was found to increase with increase in acid concentration. Maximum surface area of 1402.66 m^2/g was obtained at 40 % acid concentration.
- Proximate analysis of the activated carbon showed that the fixed carbon content of the activated carbon was quite high and the ash content was very low.
- The effect of acid concentration and activation temperature on the yield of the activated carbon was determined. The yield was found to decrease with increase in acid concentration and activation temperature.
- Iodine number, being a measure of the microporosity, implied that microporosity of the activated carbon prepared from the mixture of bael and coconut shell particles was

more (about 38%) than that of the coconut shell based activated carbon. Methylene blue number values indicated that the increase in mesoporosity of the synthesized activated carbon was quite low (around 10%). The pore volume of the newly prepared activated carbon was also found to be more than that of the coconut shell based activated carbon.

- Batch adsorption studies indicated that maximum Cr (VI) removal of 91.75% was achieved for an initial concentration of 10 mg/l for an adsorbent dosage of 10 g/l at pH=1. However, the difference in the removal efficiency was quite low (<4%) between the adsorbent dosages of 6 g/l and 10 g/l under such conditions.
- The Cr (VI) ion removal efficiency decreased with increase in pH from 1-7 and increase in initial concentration of Cr (VI) ions while it increased with increase temperature. With increase in adsorbent dosage the removal efficiency increased initially but became almost constant after a certain value.
- Langmuir, Freundlich and Temkin models were fitted to the experimental data. It was found that the isotherm data best fitted the Langmuir model with R^2=0.996.

CHAPTER 6
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6. REFERNCES

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